

San Francisco Office  
340 Brannan Street, 5th Floor  
San Francisco, CA 94107  
tel: 415-512-8800  
fax: 415-512-8982  
toll free: 1-800-829-7700  
www.translate.com  
info@polyglot.com

JP 9-12997

TRANSLATION FROM JAPANESE

- (19) JAPANESE PATENT OFFICE (JP)  
(12) Unexamined Patent Gazette (A)  
(11) Unexamined Patent Application (Kokai) No. 9-12997  
(43) Disclosure Date: January 14, 1997



(51) Int. Cl. <sup>6</sup>	Class. Symbols	Internal Office Registr. Nos.	Technical Classification Field
C 09 J 163/04	JFP	C 09 J 163/04	JFP

Request for Examination: Not yet submitted  
(Total of 5 pages [in original])

Number of Claims: 3 OL

- (21) Application No.: 7-167487  
(22) Filing Date: July 3, 1995  
(71) Applicant: 000005278 (Bridgestone Corporation)  
(72) Inventor: Kozo Sasaki  
(72) Inventor: Masaaki Nakamura  
(74) Agent: Yusuke Hiraki, Patent Attorney (and two others)

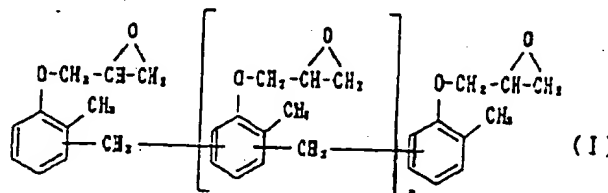
4, 9 single-dip  
ep cre-nov - ach  
Ex 16.8% ep

(54) [ Title of the Invention ] **Adhesive Composition**

(57) [ Summary ]

[ Composition ] An adhesive composition, containing a rubber latex, a thermosetting resin precondensate, and an epoxy-cresol-novolak resin expressed by Formula I below.

[ Chemical Formula 1 ]



8 No OH

[ Benefits ] Suitable for the bonding of polyester fibers and rubber, particularly heat-resistant bonding.

[ Claim 1 ] An adhesive composition, containing a rubber latex, a thermosetting resin precondensate, and an epoxy-cresol-novolak resin expressed by Formula I below.

[illegible]

[ Claim 2 ] An adhesive composition as defined in Claim 1, wherein the epoxy-cresol-novolak resin/(rubber latex + thermosetting resin precondensate) ratio, expressed as the weight ratio of solids, is confined to a range of 15/100 to 100/100.

[ Detailed Description of the Invention ]

[ Technological Field of the Invention ] The present invention relates to an adhesive composition, and more particularly to an adhesive composition suitable for the bonding of polyester fibers and rubber, particularly heat-resistant bonding.

[ Prior Art ] Polyester fiber materials, which are typified by polyethylene terephthalate and which are linear macromolecules having ester bonds in their main chains, are

common macromolecular materials having excellent initial elastic modulus, high thermal dimensional stability, and low cost, and are thus very useful in the form of filament yarns, cords, cables, cord knits, canvas, and the like as reinforcing materials for tires, belts, air springs, rubber hoses, and other rubber products.

\* { [ 0003 ] Fiber materials and rubber must be bonded to each other when such fiber materials are used for rubber product reinforcement. RFL (adhesives composed of resorcin-formaldehyde precondensates and rubber latexes) can be appropriately used in the bonding of nylon, rayon, and other fiber materials with rubber. Such RFL adhesives, however, provide very little bonding for polyester fiber materials, which are compact structurally and have few functional groups.

\* [ 0004 ] This is the reason that attempts have been made in the past to develop methods in which -OH, -COOH, -NH<sub>2</sub>, and other active groups are introduced on the polyester surface by an alkali-amine treatment in order to achieve adhesiveness with RFL solutions (for example, Japanese Examined Patent Application (Kokoku) 46-41087). With such methods, however, the fiber strength of the polyester fiber materials is unacceptably low. Similarly, isocyanate compounds or epoxy compounds are also introduced in order to achieve adhesiveness with RFL solutions (for example, Japanese Examined Patent Application 46-41087). In these methods, however, the isocyanate compounds or epoxy compounds have high reactivity and hence react with the water or resorcin-formaldehyde precondensate in the RFL. Since adhesiveness is adversely affected, bonding must be performed in two separate steps, additional equipment and steps are required, and lower operability results. In addition, the methods provide insufficient benefits in terms of energy conservation and cost. Other features of these methods include the hardening of the fiber materials subjected to bonding processes and treatments, and the impaired handling of the materials during manufacture. An even more serious drawback is that adhesiveness decreases markedly when fiber materials are used at high temperatures, the fiber materials lose some of their strength, and rubber products obtained using these as reinforcing materials have a much shorter service life. Specifically, conventional techniques involve forming a highly rigid epoxy layer on a highly rigid polyester surface, so when significant mechanical strain is exerted on a fiber material, adhesive failure occurs at the polyester-epoxy interface due to a difference in rigidity. Formation of a type of graft polymer on the surface due to the primary bonding of isocyanate compounds and epoxy compounds on the polyester surface has been cited as a reason for such a failure.

[ 0005 ] Reaction products of resorcin and triallyl cyanurate, reaction products of *p*-chlorophenyl and formaldehyde, and the like have been proposed for use in one-component bonding treatments and processes in order to overcome the aforementioned drawbacks, but these products are still inadequate because of inferior adhesion performance, lower adhesion at high temperatures, and lower strength of fiber materials. Due to increased performance requirements for modern automobiles, tires must perform better at higher speeds, and much more heat is absorbed by the polyester fiber materials. Another consideration, which is related to improved productivity, is that because tires are vulcanized at higher temperatures than in the past, heat input increases considerably not only when the products are being used (as described above) but also when they are being processed. Still another consideration, which is related to energy conservation, is that tires become progressively more lightweight and that requirements gradually become more stringent not only with respect to heat input but also with respect to mechanical input.

[ 0006 ]

[ Problems Which the Invention Is Intended to Solve ] Thus, an adhesive used for the bonding of polyester fibers and rubber must have the following characteristics: be a one-component material, not cause any reduction in the strength of fiber materials due to bonding, have high adhesiveness, produce only a small reduction in the strength of such fiber materials, lose its adhesiveness only slightly when used at high temperatures, and the like.

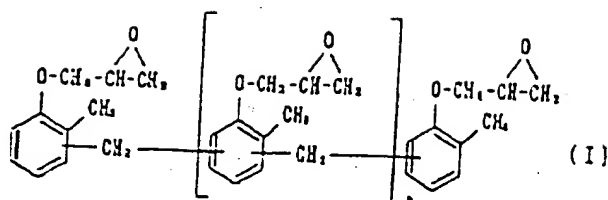
[ 0007 ]

[ Means Used to Solve the Above-Mentioned Problems ] The inventors discovered that epoxy-cresol-novolak resins, unlike the epoxy compounds conventionally used together with RFL solutions, have low reactivity at room temperature and allow bonding to be performed in a single bath (even when RFL is added) without creating problems such as those described above, and that the aforementioned drawbacks can be overcome by adding such epoxy-cresol-novolak resins to rubber latexes and thermosetting resin precondensates.

[ 0008 ] Specifically, the present invention relates to an adhesive composition containing a rubber latex, a thermosetting resin precondensate, and an epoxy-cresol-novolak resin expressed by Formula I below.

[ 0009 ]

[ Chemical Formula 2 ]



[ 0010 ] (where  $n$  is an integer from 1 to 20), as well as to an adhesive composition in which the epoxy-cresol-novolak resin/(rubber latex + thermosetting resin precondensate) ratio, expressed as the weight ratio of solids, is confined to a range of 15/100 to 100/100.

[ 0011 ] It is unsuitable for the epoxy-cresol-novolak resin/(rubber latex + thermosetting resin precondensate) ratio of the present adhesive composition, expressed as the weight ratio of solids, to decrease below 15/100, because in this case the composition adheres poorly to polyester fibers and has diminished adhesive power. Nor is it suitable for the ratio to exceed 100/100, because in this case the resin content of the adhesive composition becomes too high, the adhesive solidifies, the binding power between the adhesive and the rubber decreases, and the apparent fiber strength of a polyester fiber material decreases following bonding treatments and processes. The epoxy-cresol-novolak resin/(rubber latex + thermosetting resin precondensate) ratio, expressed as the weight ratio of solids, should preferably fall within a range of 20/100 to 100/100, and ideally within a range of 40/100 to 80/100. In addition, the thermosetting resin precondensate/rubber latex ratio, expressed as the weight ratio of solids, should preferably fall within a range of 2.5/100 to 30/100.

[ 0012 ] The thermosetting resin precondensate used in the present invention is not limited in any particular way and may be any macromolecular thermosetting resin precondensate that can be cured by heat alone or by a combination of heat and a methylene donor. Examples of such precondensates include the following precondensates, which may be used singly or as a combination of two or more components: resorcin-formaldehyde precondensates, phenol-formaldehyde precondensates, urea-formaldehyde precondensates, melamine-formaldehyde precondensates, and precondensates of formaldehyde with 3,5-xyleneol or 5-methyl resorcin.

[ 0013 ] The rubber latex used in the present invention may be any of the vinylpyridine-styrene-butadiene latexes, styrene-butadiene latexes, or natural rubber latexes commonly used on a wide scale, as well as a butyl rubber latex, a chloroprene latex, or a product obtained by dispersing compounded rubber in water or an organic solvent. These may be used singly or as a mixture of several components.

[ 0014 ] An adhesive-treated polyester fiber can be produced by depositing an adhesive composition thus configured on a fiber material such as a polyester fiber, and subjecting the product to a suitable heat treatment. The fiber thus obtained is embedded in unvulcanized rubber, and the product is vulcanized, making it possible to firmly bond the fiber and the rubber. Examples of methods in which fiber materials are deposited on adhesive compositions include methods in which fiber materials are immersed in solutions of such adhesive compositions, methods in which adhesive compositions are applied with a brush, and methods in which such adhesive compositions are sprayed. An appropriate method can be selected as needed.

[ 0015 ] The subsequent heat treatment should preferably be performed at a temperature above the glass transition temperature of the polymer in the fiber material, particularly at a temperature 20 to 70°C below the melting temperature of the polymer. The reason is that when the temperature is below the glass transition temperature of the polymer, the polymer has low molecular mobility, and it is impossible to achieve adequate interaction between the polymer and the epoxy-cresol-novolak resin contained in the adhesive composition, so the binding power between the adhesive composition and the fiber material cannot be established. Nor is it suitable for the temperature to be less than 20°C below the melting temperature of the polymer because of the deterioration of the fiber material or the latex in the adhesive composition.

[ 0016 ] The polyester fiber obtained using the adhesive composition of the present invention is commonly a linear macromolecule having ester bonds in its main chain, particular a macromolecule in which at least 25% of the bonds in the main chain are ester bonds. The polyester fiber is obtained by employing esterification reactions or ester interchange reactions to condense dicarboxylic acids (terephthalic acid, isophthalic acid, and the like) or dimethyl or other esters thereof with glycols such as ethylene glycol, propylene glycol, butylene glycol, methoxypolyethylene glycol, and pentaerythritol. Polyethylene terephthalate is the most typical polyester fiber. Such polyester fiber materials can take the shape of cords, chips, filaments, filament chips, cord knits, canvas, or the like. The adhesive composition of the present invention can also be applied to a

polyester fiber material that has been pretreated with electron beams, microwaves, corona discharges, plasma, and the like.

[ 0017 ] The adhesive composition of the present invention can be applied to the following fibers in addition to polyester fibers such as those described above: aliphatic polyamide fibers (rayon, vinylon, 6-nylon, 66-nylon, 46-nylon, and the like), aromatic polyamide fibers typified by *p*-phenylene terephthalamide, inorganic fibers typified by carbon fibers and glass fibers, and other reinforcement applications for rubber products.

The adhesive composition of the present invention is also applicable to products obtained by pretreating these fiber materials with electron beams, microwaves, plasma, or the like.

[ 0018 ] The adhesive composition of the present invention can also be applied to tires, conveyor belts, belts, hoses, air springs, and various other rubber products.

[ 0019 ]

[ Operation of the Invention ] As described above, the adhesive composition of the present invention allows polyester fibers, aliphatic polyamide fibers, aromatic polyamide fibers, inorganic fibers, and all other fiber materials to be securely bonded to rubber. The reason that the adhesive composition of the present invention is especially suitable for the bonding of polyester fiber materials and rubber is that the epoxy-cresol-novolak resin contains cresol, which has excellent solubility and dispersibility in polyester fibers, and epoxy, which reacts readily with the polyester fibers. Another reason is that epoxy-cresol-novolak resins disperse exceptionally well in polyester fibers because the molecules in these resins have a linear configuration. Yet another reason is that because the skeleton of an epoxy-cresol-novolak resin has high methylation reactivity or reactivity toward methylene cross-linking, it reacts efficiently with the thermosetting resin precondensate in the adhesive composition, demonstrating a pronounced reinforcing effect in relation to the adhesive composition.

[ 0020 ]

[ Working Examples ] The present invention will now be described in further detail through working and comparative examples, but the scope of the present invention is not limited by these.

Comparative Example 1 The fiber material used was a cord obtained by twisting a polyethylene terephthalate weaving yarn with a fineness of 1500 denier at 40 primal twists per 10 centimeters and 40 final twists per 10 centimeters.

[ 0021 ]

[ Table 1 ]

Diglycerol triglycidyl ether	1.20 weight parts
Sodium dioctyl sulfosuccinate	0.02 weight part
Caustic soda (10% aqueous solution)	0.14 weight part
Soft water	98.64 weight parts

[ 0022 ]

[ Table 2 ]

Soft water	518.59 weight parts	
Resorcin	15.12 weight parts	RF 21.31Σ
Formaldehyde (37% aqueous solution)	16.72 weight parts	6.19 pbw
Caustic sodium (10% aqueous solution)	11.00 weight parts	
Vinylpyridine-styrene-butadiene latex (concentration: 41%)	216.58 weight parts	88.8 pbw
Styrene-butadiene latex (concentration: 40%)	221.99 weight parts	88.8 pbw

[ 0023 ]

[ Table 3 ]

Natural rubber	80 weight parts
Styrene-butadiene copolymer rubber	20 weight parts
Carbon black	40 weight parts
Stearic acid	2 weight parts
Petroleum-based softener	10 weight parts
Pine tar <sup>1</sup>	4 weight parts
Zinc bloom	5 weight parts
N-phenyl-β-naphthylamine	1.5 weight parts
2-Benzothiazyl disulfide	0.75 weight part
Diphenyl guanidine	0.75 weight part
Sulfur	2.5 weight parts

The above-described fiber material was immersed in the adhesive composition described in Table 1, dried for 1.5 minutes at 150°C, heat-treated for 1 minute at 240°C,

<sup>1</sup> Translator's note: Literally "bine tar," which appears to be a typographical error.



immersed in the adhesive composition described in Table 2, dried for 1.5 minutes at 150°C, and heat-treated for 2 minutes at 240°C, yielding an adhesive-treated cord.

[ 0024 ] This adhesive-treated cord was embedded in the unvulcanized rubber shown in Table 3, and vulcanized for 30 minutes at a temperature of 170°C and a pressure of 20 kg/cm<sup>2</sup>. The cord was raised from the resulting vulcanization product, and the reaction developed during the peeling of the cord from the vulcanization product at a velocity of 30 cm/min was termed initial adhesive power. The results are shown in Table 5. The adhesive-treated cord was embedded in the same manner in the unvulcanized rubber shown in Table 3 and vulcanized for 45 minutes at a temperature of 190°C and a pressure of 20 kg/cm<sup>2</sup>. A vulcanization product was manufactured by the same method, and the resistance measured by the same method was termed heat-resistant adhesive power. The results are also shown in Table 5.

[ 0025 ] A vulcanization product obtained by the same method as the one used to measure the initial adhesive power was kept for 10 minutes in a thermostat in which a 120°C environment was maintained, and the resistance measured directly in the thermostat by the same method was termed high-temperature adhesive power. The results are also shown in Table 5.

Working Examples 1-5, Comparative Examples 2 and 3 ARALDITE: ECN 1400<sup>®</sup> manufactured by Asahi Chiba was used as the epoxy-cresol-novolak resin, and a resin solution whose composition is shown in Table 4 was prepared.

[ 0026 ]

[ Table 4 ] Resin solution

Epoxy-cresol-novolak resin (40% dispersion)	500.00 weight parts
Sodium dioctyl sulfosuccinate	2.86 weight parts
Caustic sodium (10% aqueous solution)	0.60 weight part
Soft water	496.54 weight parts

50.1%  
200 pw

The adhesive composition shown in Table 2, that is, the RFL solution, was mixed with this resin solution in the ratios shown in Table 5, yielding adhesive compositions.

[ 0027 ] The fiber material used in Comparative Example 1 was prepared, immersed in the adhesive compositions, dried for 1.5 minutes at 150°C, and heat-treated for 2 minutes at 240°C, yielding an adhesive-treated cord. This adhesive-treated cord was measured for

initial adhesive power, heat-resistant adhesive power, and high-temperature adhesive power in the same manner as in Comparative Example 1. The results are shown in Table 5.

[ 0028 ]

[ Table 5 ]

16.8% epoxy

		Comparative Example 1	Comparative Example 2	Working Example 1	Working Example 2	Working Example 3	Working Example 4	Working Example 5	Comparative Example 3
Adhesive composition	RFL solution added*1		909.09	833.33	714.29	625.00	555.56	500.00	454.55
	Resin solution added*1		90.91	166.67	285.71	375.00	444.44	500.00	545.45
Epoxy-cresol-novolak resin/(resorcin-formaldehyde precondensate + rubber latex) weight ratio*2			10/100	20/100	40/100	60/100	80/100	100/100	120/100
Initial adhesive power (kg)		2.64	2.66	2.62	2.67	2.70	2.72	2.69	2.41
Heat-resistant adhesive power (kg)		1.17	1.19	1.33	1.43	1.60	1.52	1.35	0.98
High-temperature adhesive power (kg)		1.05	1.02	1.19	1.36	1.41	1.35	1.12	0.85

\*1: Weight of solids

\*2: Weight ratio of solids

Ex | RFL solution 833.33  
Resin solution 166.67

[ 0029 ]

[ Merits of the Invention ] The present invention can provide an adhesive composition suitable for the bonding of polyester fibers and rubber, particularly to heat-resistant bonding.